New standardised analytical methods meeting WFD requirements - results of a mandated project of the European Commission (M424)

Ulrich Borchers

(IWW Water Centre, DE)

Edinburgh, 24th - 25th November 2014
(Can We Afford NOT to Monitor Priority Pollutants?)

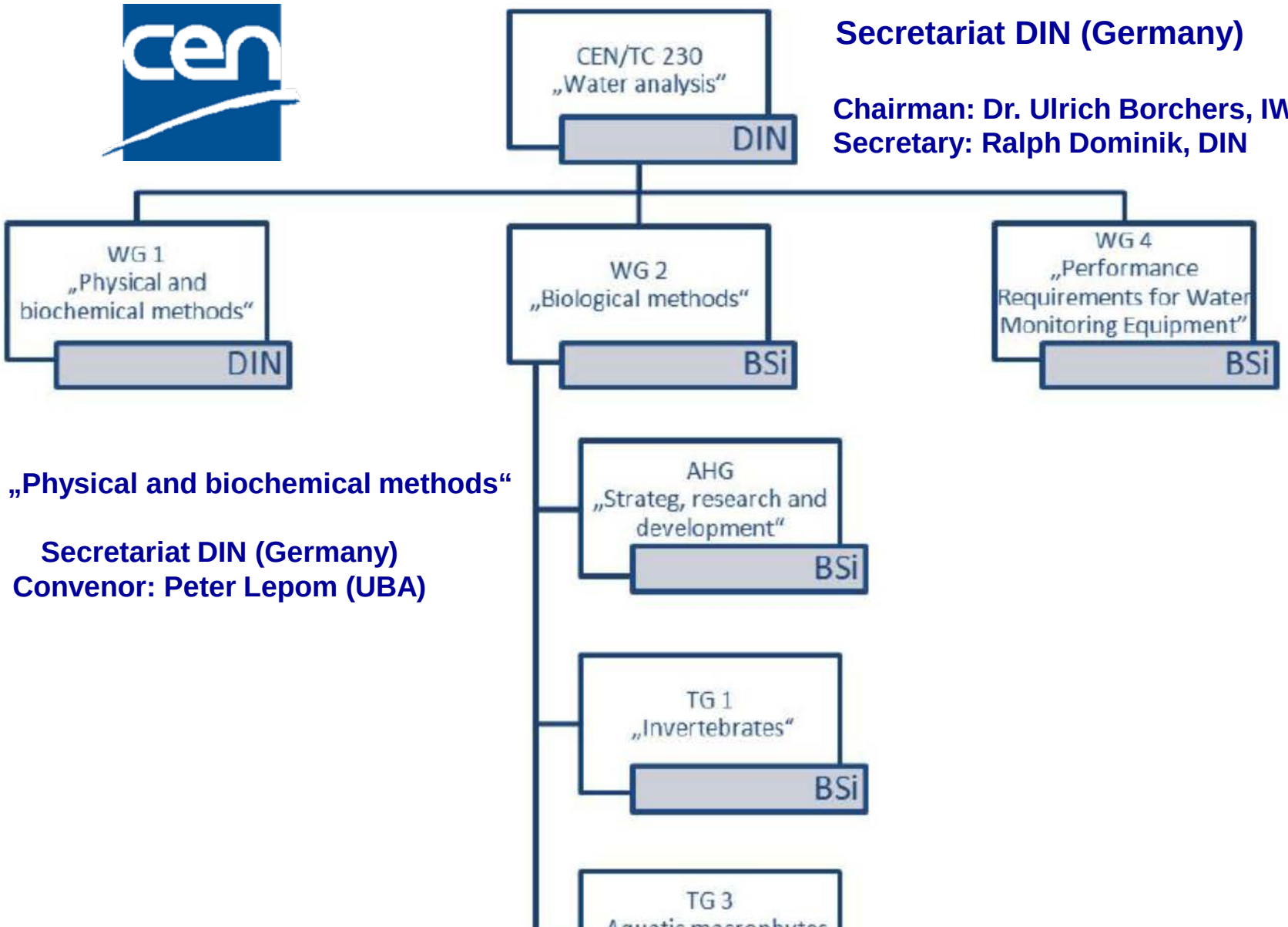
IWW Rheinisch-Westfälisches Institut für Wasser Beratungs- und Entwicklungsgesellschaft mbH

Institut an der Universität Duisburg Essen

Topics

- **Introduction and Background**
- **The Mandate M424**
  - Content
  - Requirements
  - Execution
- **The 5 Chemical Projects**
  - Methods
  - Performance Data
  - Status
- **Further Steps**
  - Watchlist
  - Method Proposals WG Chemicals (JRC IES)

CEN TC 230 „Water Analysis“



Secretariat DIN (Germany)

Chairman: Dr. Ulrich Borchers, IWW
Secretary: Ralph Dominik, DIN

WG 1 „Physical and biochemical methods“

Secretariat DIN (Germany)
Convenor: Peter Lepom (UBA)

QA/QC Commission Directive (2009/90/EC)

L 201/36 EN Official Journal of the European Union 1.8.2009

COMMISSION DIRECTIVE 2009/90/EC

of 31 July 2009

laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status

(Text with EEA relevance)

- **Published:**
  - **1st August 2009**
- **Objectives**
  - **Provision of data of proper scientific quality**
    - **Basis for all programme of measures**
  - **Comparability of monitoring results across Europe**
    - **Implementation of common principles and harmonised procedures for chemical monitoring**





QA/QC Commission Directive (2009/90/EC)

- **Standardised and other validated methods**
  - Any method provided it is properly validated and meets certain performance criteria may be applied
- **Requirements on analytical methods**
  - Validation according to EN ISO 17025
  - Limit of Quantification (LOQ)
    - ≤ 30 % of the relevant EQS
  - Relative Target Uncertainty at EQS level
    - ≤ 50 %
- **If there is no EQS or no method that meets the performance criteria**
  - best available techniques
  - not entailing excessive costs

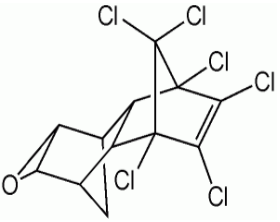
Analytical Challenges (problematic parameters)

- **European Survey on performance criteria for relevant methods by CEN**
  - European Expert groups
  - Reference laboratories
  - Competent Authorities

- **Main conclusion (2008)**
  - Monitoring of EQC compliance for about 25% of priority substances hardly possible due to
    - poor methods
    - or missing definitions/descriptions
  - For some of the substances suitability of the respective methods was not proven for whole water samples
    - Lack of validation data

Priority Substances Difficult to Analyse

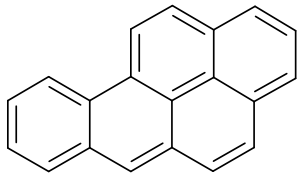
Organochlorine pesticides



Dieldrin

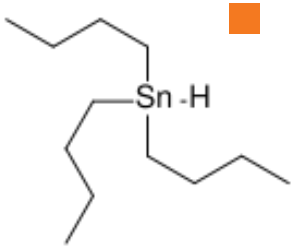
- **Sensitivity insufficient for cyclodiene pesticides, endosulfane, and pentachlorobenzene**
- **Difficulties in meeting required LOQ for DDT, hexachlorocyclohexane and hexachlorobenzene**

Polycyclic Aromatic Hydrocarbons



- **Sensitivity insufficient for Indeno[1,2,3-cd]pyrene and benzo[ghi]perylene compounds as the LoQ**
- **Difficulties in meeting required LOQ for benzo[k]fluoranthene and benzo[b]fluoranthene**

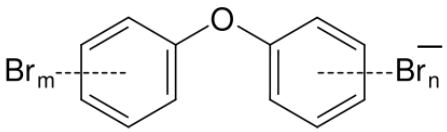
Tributyl tin compounds



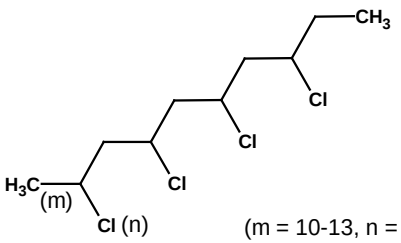
- **Requirements on LOQ impossible to achieve since AA-EQS is 0.2 ng/L**
- **Lowest reported LoQ was about 1 ng/L**

Priority Substances Difficult to Analyse

- **Pentabromodiphenylether**
  - No standardised method for water available
  - Requirements on LOQ hard to meet
  - the sum concentration of 6 congeners has to be below 0.5 ng/L and 0.2 ng/L, respectively (AA-EQS IW, OW)



- **Short-chain chlorinated paraffins**
  - No standard method for water available in 2009
  - Analysis not under control also in research laboratories
  - Most frequently applied method was GC-ECNI-MS



(m = 10-13, n = 1-13)

Unsolved Problems:

- Calibration, dependency of response on degree of chlorination
- Isomers with less than five chlorine cannot be detected

Topics

- Introduction and Background
- The Mandate M424
  - Content
  - Requirements
  - Execution
- The 5 Chemical Projects
  - Methods
  - Performance Data
  - Status
- Further Steps
  - Watchlist
  - Method Proposals WG Chemicals (JRC IES)

The Way out: Edition of a Mandate to CEN

- **Mandate edited under the number M/424**
  - **Development or improvement of standards in support of the WFD**

EUROPEAN COMMISSION
ENTERPRISE AND INDUSTRY DIRECTORATE-GENERAL

New Approach Industries, Tourism and CSR
Director

07 AVR. 2008

Brussels,
ENTR/I3/RG/kk D(2008)10160

Mr Gaston Michaud
Secretary General
CEN
Rue Stassart 36
B-1050 Brussels

Subject: **M/424 Mandate addressed to CEN for the development or improvement of standards in support of the Water Framework Directive**

Mandate M/424

- **Requirements according to QA/QC directive and to other WFD aspects**

  - Analysis of **whole water samples**
  - The methods should enable the analysis of samples containing up to **0.5 g/L of suspended solids**
  - **Limits of quantification** – equal or less than 30% EQS
  - **Measurement uncertainty** – equal or less than 50%
  - Method should be fully in-house validated
  - Validation by European intercomparison studies according to ISO 5725

Mandate M 424

- **September 2012**
  - Kick-off meeting
- **November 2013**
  - Draft standards were circulated for CEN enquiry
- **June/July 2014**
  - Interlaboratory comparisons acc. ISO 5725
- **October 2014**
  - Presentation of validation data and final comments
  - All 5 methods ready for publication as EN (EN/TS)
- **April → August 2015**
  - All Standards published

Topics

- Introduction and Background
- The Mandate M424
  - Content
  - Requirements
  - Execution
- The 5 Chemical Projects
  - Methods
  - Performance Data
  - Status
- Further Steps
  - Watchlist
  - Method Proposals WG Chemicals (JRC IES)

The new standards

BS EN 16691:2015-08

- Water quality — Determination of polycyclic aromatic hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas chromatography mass spectrometry (GC-MS)

- Responsible project leader
  - TNO, The Netherlands

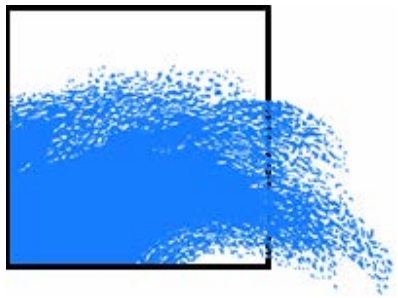
TNO innovation for life

The new standards

CEN/TS 16692:2015-04

- Water quality — Determination of tributyl tin (TBT) in whole water samples using solid phase extraction (SPE) and gas chromatography with triple quadrupole mass spectrometry

- Responsible project leader
  - MUMM, The Management Unit of the North Sea Mathematical Models and the Scheldt estuary, Belgium



The new standards

BS EN 16693:2015-08

- Water quality — Determination of organochlorine pesticides (OCP) in whole water samples using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)

- Responsible project leader
  - IWW Water Centre Germany

The new standards

BS EN 16694:2015-08

- Water quality — Determination of pentabromodiphenyl ether (PBDE) in whole water samples using solid phase extraction (SPE) with SPE-disks combined with gas chromatography - mass spectrometry (GC-MS)

- Responsible project leader
  - VITO, Belgium

vito
vision on technology

The new standards

BS EN ISO 16692

- Water quality - Determination of short-chain polychlorinated alkanes (SCCPs) in water - Method using gas chromatography-mass spectrometry (GC-MS) and negative-ion chemical ionization (NCI)

- Responsible project leader
  - Under ISO TC 147 lead

New validation method CEN/TS 16800

- **In parallel to the methods a validation guideline was developed under WG 1 of CEN TC 230**

TECHNICAL SPECIFICATION

SPÉCIFICATION TECHNIQUE

TECHNISCHE SPEZIFIKATION

CEN/TS 16800

December 2015

ICS 13.060.50

English Version

Guideline for the validation of physico-chemical analytical methods

Topics

- Introduction and Background
- The Mandate M424
  - Content
  - Requirements
  - Execution
- The 5 Chemical Projects
  - Methods
  - Performance Data
  - Status
- Further Steps
  - Watchlist
  - Method Proposals WG Chemicals (JRC IES)

European Commission

EMRP-ENV08-WP5: Preparation of Reference Materials: Results & Conclusions

EURAMET
European Association of National Metrology Institutes




Saioa Elordui
Håkan Emteborg

Joint Research Centre – Institute for Reference Materials and Measurements

EMRP
European Metrology Research Programme
Programme of EURAMET

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Validation Intercomparison – PAHs

- **Participants: 18**
- **Samples:**
  - **S1: Low level samples containing SPM**
  - **S2: High level samples containing SPM**
  - **S3: Sample without SPM to be spiked with the supplied solution**
- **Preparation of SPM containing samples: IRMM**
- **Matrix used for preparing samples: mineral water**
- **Two procedural blanks were requested**

Conclusion (1)

- **Feasibility proven that is possible to prepare SPM containing samples with measurand concentrations in the pg/L or low ng/L range**

- **PAH (BS EN 16691)**
  - **Method OK for samples with low and high SPM content**
  - **Reproducibility between 8% and 48% (samples with SPM)**
  - **Required LOQ difficult to achieve for**
    - **Indeno[1,2,3-cd]pyrene**
    - **benzo[ghi]perylene**

Method meets WFD requirements for most parameters

Conclusion (2)

- **TBT (CEN/TS 16692)**
  - Method OK for samples with low and high SPM content
  - Low number of participants
  - Blank values in the range of EQS (0.3 ng/l)
  - Reproducibility between 31% and 53% (samples with SPM)
  - Requirements of WFD as regards LoQ were not met
- **OCP (BS EN 16693)**
  - Method OK for samples with low and high SPM content
  - Reproducibility between 20% and 61% (samples with SPM)
  - Problems wit LOQ and Uncertainty for a few parameters

Method meets WFD requirements for most parameters

Conclusion (3)

- **PBDEs (BS EN 16694)**
  - Method OK for samples with low and high SPM content
  - Reproducibility between 14% and 36% (samples with SPM)

  Blank problems in some laboratories

  Method meets WFD requirements

- **CEN /TS 16800**
  - Good guideline for validation purposes
  -

- **Further information on the methods and the performance data (validation trials) can be provided**
  - Please contact me
  - u.borchers@iww-online.de

Topics

- Introduction and Background
- The Mandate M424
  - Content
  - Requirements
  - Execution
- The 5 Chemical Projects
  - Methods
  - Performance Data
  - Status
- Further Steps
  - Watchlist
  - Method Proposals WG Chemicals (JRC IES)

Analysis of Watch List Parameters?

- **1st Watch List under the Environmental Quality Standards Directive (Directive 2008/105/EC as amended by Directive 2013/39/EU (EQSD)**
  - **New mechanism to provide monitoring information on the concentrations of potentially polluting substances in the aquatic environment**
  - **To support future prioritisation**
  - **Process involves a Watch List with a limited number of substances and monitoring them EU-wide for up to 4 years**
  - **Maximum number of 10 substances or groups of substances shall be included**
  - **Increasing by one at each update, up to a maximum of 14 substances or groups of substances**

1st Watch List under the EQSD

- **COMMISSION IMPLEMENTING DECISION (EU) 2015/495 of 20 March 2015**
  - 17-Alpha-ethinylestradiol (EE2)
  - 17-Beta-estradiol (E2), Estrone (E1)
  - Diclofenac
  - 2,6-Ditert-butyl-4-methylphenol
  - 2-Ethylhexyl 4-methoxycinnamate
  - Macrolide antibiotics
  - Methiocarb
  - Neonicotinoids
  - Oxadiazon
  - Tri-Allate

Issue for further standardisation?